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(54) Method and arrangement for drying substrates after treatment in a liquid.

(57) A method and an arrangement for treating substrates, such as, for example, silicon wafers (1), in which the latter are immersed for some time in a bath (2) containing a liquid (3) and are then taken therefrom so slowly that practically the whole quantity of liquid remains in the bath (2). According to the invention, the substrates (1) are brought from the liquid (3) directly via leads (17) with outlet nozzles (18) into contact with a vapour not condensing thereon of a substance miscible with the liquid (3), which, when mixed therewith, yields a mixture having a surface tension lower than that of the liquid. It has been found that no drying marks with organic or metallic residues or other contaminations then remain on the substrates (1).

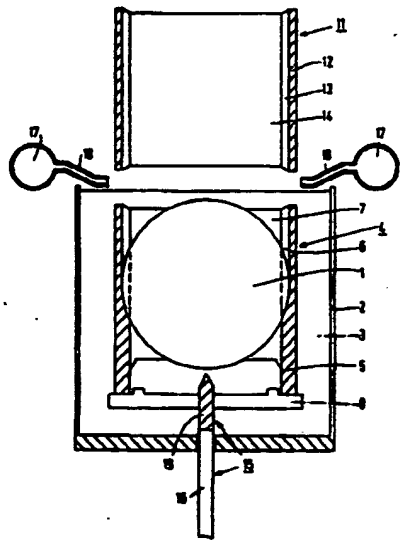

FIG.2

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Method and arrangement for drying substrates after treatment in a liquid.

The invention relates to a method of treating substrates, in which the latter are immersed for some time in a bath containing a liquid and are then taken therefrom so slowly that practically the whole quantity of liquid remains in the bath. The invention also relates to an arrangement for carrying out such a method.

A method of this kind may be used, for example, in the manufacture of electric circuits on all kinds of substrates, such as, for example, integrated circuits on semiconductor wafers (for example of silicon), drives for liquid crystal displays on transparent plates of glass or quartz or circuits on plates of synthetic material (circuit boards). The method may also be used in the manufacture of shadow masks for television picture tubes or in the manufacture of CD or VLP records. In all these cases, the substrates are immersed many times for some time in a bath containing a liquid, for example in galvanic baths for deposition of metals, in etching baths for etching patterns into metal layers or into semiconductor material, in development baths for developing exposed photolacquer layers and in rinsing baths for cleaning the substrates. After treatment in the liquid baths, the substrates are taken from the liquid and are dried. The substrates can be taken from the liquid in that they are lifted or withdrawn from the liquid, but of course also in that the liquid is caused to flow out of the bath.

US PS No. 4,722,752 discloses a method of the kind mentioned in the opening paragraph, in which silicon wafers are immersed for some time for cleaning in a liquid containing hot (90 °C) deionized water. Subsequently, the silicon wafers are lifted from the water slowly (at a speed of about 5 cm/min. This speed is sufficiently low to ensure that the silicon wafers leave the bath in practically dry state. The surface tension then should play a part.

It has been found in practice that in this method of drying contaminations from the liquid can remain on the substrates. It has been found that with the use of the known method described a water film having a thickness of a few microns remains on the silicon wafers. This water film then evaporates rapidly, but this may give rise to so-called "drying marks". During drying, the water film can be contracted so that contaminations in the water, which are often of organic or metallic nature, remain in local concentration on the wafers. Such residues can be very disturbing if, for example, the wafers must still be subjected to an etching treatment. They can locally delay the etching treatment or even prevent this treatment. Further, of course dust particles present in the water film also remain on the wafers.

The invention has inter alia for its object to provide a method, in which the said disadvantages are obviated.

For this purpose, according to the invention, the method mentioned in the opening paragraph is characterized in that the substrates are brought directly from the liquid into contact with a vapour not condensing thereon of a substance, which is miscible with the liquid and yields, when mixed therewith, a mixture having a surface tension lower than that of the liquid. It is then a surprise to find that, after the substrates have been dried in this manner, no drying marks and contaminations are present any longer on these substrates. Further, experiments have shown that, if nevertheless a liquid film remains on the substrates, this film must be thinner than 3 nm.

It is presumed that the much more satisfactory drying with the use of the method according to the invention, in which apparently a much smaller quantity of liquid or no liquid remains on the substrates, is obtained by the Marangoni effect. If a lyophilic substrate is partly immersed in a liquid, the liquid constitutes at the substrate a concave meniscus. A liquid film having a thickness increasing in the direction of the liquid bath is then present on the substrate. If such a liquid film is brought into contact with a vapour not condensing on the substrate of a substance miscible with the liquid, this substance will be mixed with the liquid in the film in such a manner that its concentration therein initially decreases in the direction of the liquid bath. The concentration of the substance then exhibits a gradient in the liquid film. Since, when mixed with the liquid, the substance yields a mixture having a surface tension which is lower than that of the liquid, the gradient in the concentration will result in a gradient in the surface tension in the liquid film. By this gradient an additional force is exerted on the liquid film in the direction of the liquid bath (Marangoni effect). Thus, a more satisfactory drying of the substrates is obtained.

In th method according to the invention, the vapour does not condense on th substrates. If this should be the case, the substrates would be covered, after having been taken from the liquid, with a layer of condensed vapour. Of course, such a layer must also be removed, as a result of which the drying process will take more time. Further, such a layer can attack the substrate. This is the case, for example, if the layer contains an organic solvent and if the substrate is provided, for example, with a photolacquer pattern. In practice, also more dust particles will remain on the substrates after drying thereof. An experiment with a vapour condensing on the substrates showed that about ten times more dust particles were present on the

substrates than with a vapour not condensing thereon. A vapour not condensing on the substrates has a vapour pressure which is not saturated at the temperature of the bath and th substrates, whereas a vapour condensing on the substrates indeed has such a saturated vapour pressure.

As already stated above, substrates can be treated in different liquid baths. In practice, however, these baths mostly contain water. In this case, preferably an organic solvent is used as a substance miscible with the liquid. It has been found that many alcohols, glycols, aldehydes, esters and ketones, but also a solvent, such as tetrahydrofurane, can ensure that the substrates are dried satisfactorily. The method according to the invention can also be utilized successfully if the said baths contain other liquids, such as for example, alcohol. The substrates may be brought directly from alcohol into contact with the vapour of the organic solvent 1,1,1-trifluorotrichloroethane in order to obtain a satisfactory drying.

If the bath in which the substrates are immersed for some time contains water, according to the invention, use is preferably made of an organic solvent having a solubility in water which is higher than 1 g/l and having a vapour pressure lying between 25 and 25,000 Pascal. Experiments have shown that in these conditions satisfactory drying results are obtained. If the solubility in water is lower than the said amount, evidently too little vapour is taken up by the liquid to cause a surface tension gradient which is sufficiently large to obtain the desired drying. If the vapour pressure is lower than the said lower limit, evidently a sufficient quantity of vapour is not taken up by the liquid either. If the vapour pressure is higher than the said upper limit, such a large quantity of vapour is taken up by the liquid that also in this case evidently a surface tension gradient is obtained which is too small to obtain the desired drying.

The substrates can be taken from water comparatively rapidly (at a speed up to 1.5 cm/sec) if according to the invention an organic solvent is used from the group comprising ethyl glycol, 1-propanol, 2-propanol and tetrahydrofurane.

If substrates covered with a layer of photolacquer are taken from water (for example after development), 2-propanol is preferably used as organic solvent. The photolacquer is practically not attacked by this vapour.

Preferably, the substrates are brought into contact with the vapour by mixing the vapour with a carrier gas and by passing this mixture over the liquid. Thus, the vapour can be brought locally and in high concentration into contact with the substrates. The pressure of the vapour can then be chosen so that the said condensation thereof on the substrates is readily avoided.

When substrates, for example silicon wafers, are taken from a liquid and are brought into contact, as described above, with a suitable vapour in that they are partly carried above the liquid by means of a lifting member present in the liquid, those parts which then project above the liquid will be dry. If the substrates are then gripped at these dry parts and are further lifted out of the liquid, a drop of liquid can stick to those parts of the substrates which are the last to leave the liquid. Such a drop of liquid at the edge of an otherwise dry substrate need not be objectionable, but may give rise to problems already mentioned above. It is a surprise to find that the formation of such drops is avoided if according to the invention, when taking the substrates from the liquid, those parts thereof which are the last to leave the liquid are supported when leaving the liquid by a knife-shaped member. The said drops then flow away to this knife-shaped member. It is particularly practical if the substrates are lifted from the liquid by means of the knife-shaped member.

The invention further relates to an arrangement for carrying out the method mentioned in the opening paragraph, this arrangement being provided with a lifting member for lifting the substrates above the liquid and with means for gripping the dry substrates above the liquid.

Such an arrangement is known from US PS No. 4,722,752, in which the lifting member lifts the substrates partly out of the liquid, whereupon the substrates are gripped at their dry parts and are further lifted from the liquid by a substrate cassette. The lifting member then remains under the liquid so that wet parts of the substrates, when leaving the liquid, are in contact neither with the lifting member nor with the substrate cassette. At such contact areas drops of liquid could be left behind.

In order to obtain a satisfactory drying of the substrates, the latter are brought into contact, as described above, immediately upon leaving the liquid with a vapour not condensing thereon of a substance which, when mixed with a liquid, yields a mixture having a surface tension lower than that of the liquid. For this purpose, the arrangement according to the invention is provided with leads with outlet openings to bring this vapour into the desired contact with the substrates.

On the lower side of the substrates, which in the known arrangement are taken from the liquid, the drop of liquid sticks. In order to avoid this, the arrangement according to the inventi n is provided with a knife-shaped member, which supports the substrates when lifted from the liquid at those parts of the substrates which are the last to leave the liquid. The said drops then flow away via the knife-shaped member.

Preferably, the knife-shaped member is provided on the lifting member so that the substrates are lifted fr m the liquid by the knife-shaped member. Thus, a practical and simple arrangement is obtained.

The invention will now be described more fully, by way of example, with reference to a drawing and a few embodiments. In the drawing:

Figure 1 is a diagrammatic longitudinal sectional view f the arrangement according to the invention,

Figure 2 shows a cross-section of the arrangement shown in Figure 1 taken on the line I-I, and

Figures 3 to 6 show diagrammatically a few stages of carrying out the method according to the invention by means of the arrangement shown in Figures 1 and 2.

Figures 1 and 2 show diagrammatically an arrangement for carrying out a method for treating substrates 1, in which these substrates are immersed for some time in a bath 2 containing a liquid 3 and are then taken therefrom so slowly that practically the whole quantity of liquid 3 remains in the bath 2. Although this method may be used for treating all kinds of substrates, such as plates of glass, quartz or synthetic material, in this example silicon wafers are treated. If semiconductor devices, such as transistors, diodes or integrated circuits, are manufactured on such wafers, these wafers are immersed many times for some time in a bath containing liquid, for example in an etching, development or cleaning bath. After these treatments, the wafers 1 are taken from the liquid 3 and are dried.

In the arrangement shown in Figures 1 and 2, the substrates are immersed in the liquid 3. They are arranged in a teflon cassette 4 having side walls 5 which are provided with grooves 6 for receiving the substrates 1. The side walls 6 are interconnected by transverse walls 7. The cassette 4, which is not shown so as to be crowded with substrates for the sake of clarity, can often comprise in practice a considerably larger number of substrates than is shown in the drawing. The cassette 4 bears in the liquid 3 on two supporting arms 8, which can be moved upwards by means of shafts 9, which are passed through the bottom 10 of the bath 2 and are driven by driving means not shown so that the cassette 4 can be lifted out of the liquid 4. Above the liquid 3, an auxiliary cassette 11 is arranged having side walls 12 which are provided with grooves 13 for receiving the substrates 1. The side walls 12 are interconnected by transverse walls 14. The auxiliary cassette 11 can move vertically up and down, guided by guides not shown in the drawing for the sake of clarity. In its lowermost position, it is located, as shown in Figures 1 and 2, at a small distance from the liquid 3.

Further, the arrangement comprises a lifting member 15, which can be moved upwards by means of shafts 16, which are passed through the bottom 10 of the bath 2 and are driven by driving means not shown. Thus, the substrates 1 can be slipped from the cassette 4 into the auxiliary cassette 11.

The arrangement also comprises gas leads 17 with outlet nozzles 18 to bring the substrates 1, when they are slipped from the cassette 4 into the auxiliary cassette 11, immediately after leaving the liquid 3 into contact with a vapour of a substance which can be mixed with the liquid and yields, when mixed therewith, a mixture having a surface tension lower than that of the liquid 3. The substrates, which are then lifted in dry state from the liquid, are gripped above the liquid by the auxiliary cassette 11.

Figures 3 to 6 show diagrammatically a few stages of carrying out the method according to the invention by means of the arrangement described above.

Figure 3 again shows the stage already shown also in the arrangement of Figures 1 and 2. The substrates 1 are located under the liquid 3 in the cassette 4. The substrates 1 are taken from the liquid after having been immersed in the liquid for some time in that they are slipped by means of the lifting member 15 from the cassette 4 into the auxiliary cassette 13, as is indicated in Figures 4 and 5. Subsequently, the cassette 4 is lifted from the liquid, this cassette taking along the auxiliary cassette 11, which is vertically movable, as indicated in Figure 6. The cassette 4, which leaves the liquid in dry state because it is made of a hydrophobic material, can then be removed with the dry substrates 1.

The substrates 1 are taken so slowly from the liquid 3 that practically the whole quantity of liquid remains in the bath. According to the invention, the substrates 1 are brought directly from the liquid 3 into contact with a vapour not condensing thereon of a substance miscible with the liquid, which, when mixed therewith, yields a mixture having a surface tension lower than that of the liquid. It has been found that the substrates 1 then substantially do not exhibit drying marks or other contaminations. If the substrates 1 are taken by means of the arrangement described above from a bath containing water without the said vapour being supplied, it has been found that a water film having a thickness of a few microns remains on the substrates 1. This film evaporates rapidly, it is true, but drying marks and other contaminations from the water film then remain on the substrates 1. Th drying marks generally comprise organic and metallic residues, which may be very disturbing when further processing the substrates.

In practice, the liquid 3 in the bath 2 is often water. Preferably, an organic solvent is then used as the substance miscible with the liquid. It has been found that many alcohols, aldehydes, esters and ketones and, for example, also tetrahydrofurane can cause the substrates to be dried satisfactorily. Preferably, an organic solvent is further used having a solubility in water which is higher than 1 g/l and having a vapour pressure lying between 25 and 25,000 Pascal. As will appear from the embodiments, satisfactory drying

results are then obtained. If the solubility is lower than the said amount or if the vapour pressure lies outside th said range, the drying is l ss satisfactory and, as will also appear, drying surfaces can then be observed on the treated substrates.

The substrates can be taken from water comparatively rapidly (at a speed of up to 1.5 cm/sec) if according to the invention an organic solvent from the group comprising ethyl glycol, 1-propanol, 2-propanol and tetrahydrofurane is used.

If substrates covered with a layer of photolacquer are taken from water, for example from a development bath, preferably 2-propanol is used as the organic solvent. The photolacquer is then practically not attacked.

Preferably, the substrates 1 are brought into contact with the vapour in that the latter is mixed in a usual manner with a carrier gas and in that then this mixture is passed through the leads 17 and the outlet nozzles 18 over the liquid 3. Thus, the vapour can be supplied locally and in high concentration without condensation of the vapour on the substrates 1 taking place.

As will appear from the Figures, when taking the substrates 1 from the liquid 3, those parts which are the last to leave the liquid 3 are supported when leaving the liquid 3 by a knife-shaped member 19. According to the invention, this knife-shaped member 19 forms parts of the lifting member 15 and the substrates are lifted from the liquid by the knife-shaped member 19. The knife-shaped member 19 is made, for example, of quartz glass and has an apical angle of less than 100°. When the substrates are lifted from the liquid 3, the whole quantity of liquid now flows away via this knife-shaped member 19. If at the stage of the method shown in Figure 4 the substrates 1 should be gripped at their dry parts and should be further lifted from the liquid 3, a drop of liquid would stick to the substrates 1. Just this last drop flows away via the knife-shaped member 19. As will further also appear from the Figures, when the substrates 1 leave the liquid 3 there is no contact between the wet parts of these substrates with the cassette 1 and with the auxiliary cassette 11. If this should be the case, at the areas at which there was such a contact drops of liquid could stick.

Embodiments.

In the manner described above, silicon wafers - which were cleaned before in a usual manner in a U.V. ozone cabinet -were immersed in water and were then lifted therefrom at a speed of about 1 mm/sec. The water was intentionally strongly contaminated to a 1 M NaCl solution. The substrates were brought into contact, when leaving the liquid, directly with the vapour not condensing thereon of different solvents which are miscible with water and yield a mixture having a surface tension which is lower than that of water in that about 0.5 l of nitrogen is passed per second through a washing flask containing the organic solvent and in that then the gas mixture is passed over the liquid via the leads 17 and the outlet nozzles 18. In the following table, the results of these experiments are indicated. In the column "result", "+" indicates that under a microscope with a magnification of 500 times no drying marks can be observed on the substrates, whereas "-" indicates that such marks can be observed. Further, the vapour pressure and the solubility of the examined organic solvents are indicated in the table. It has been found that these two quantities must lie within the limits already indicated above in order to obtain a satisfactory drying of the substrates. The complete solubility mentioned in the table means that mixtures can be formed having a concentration between 0 and 100% of organic solvent.

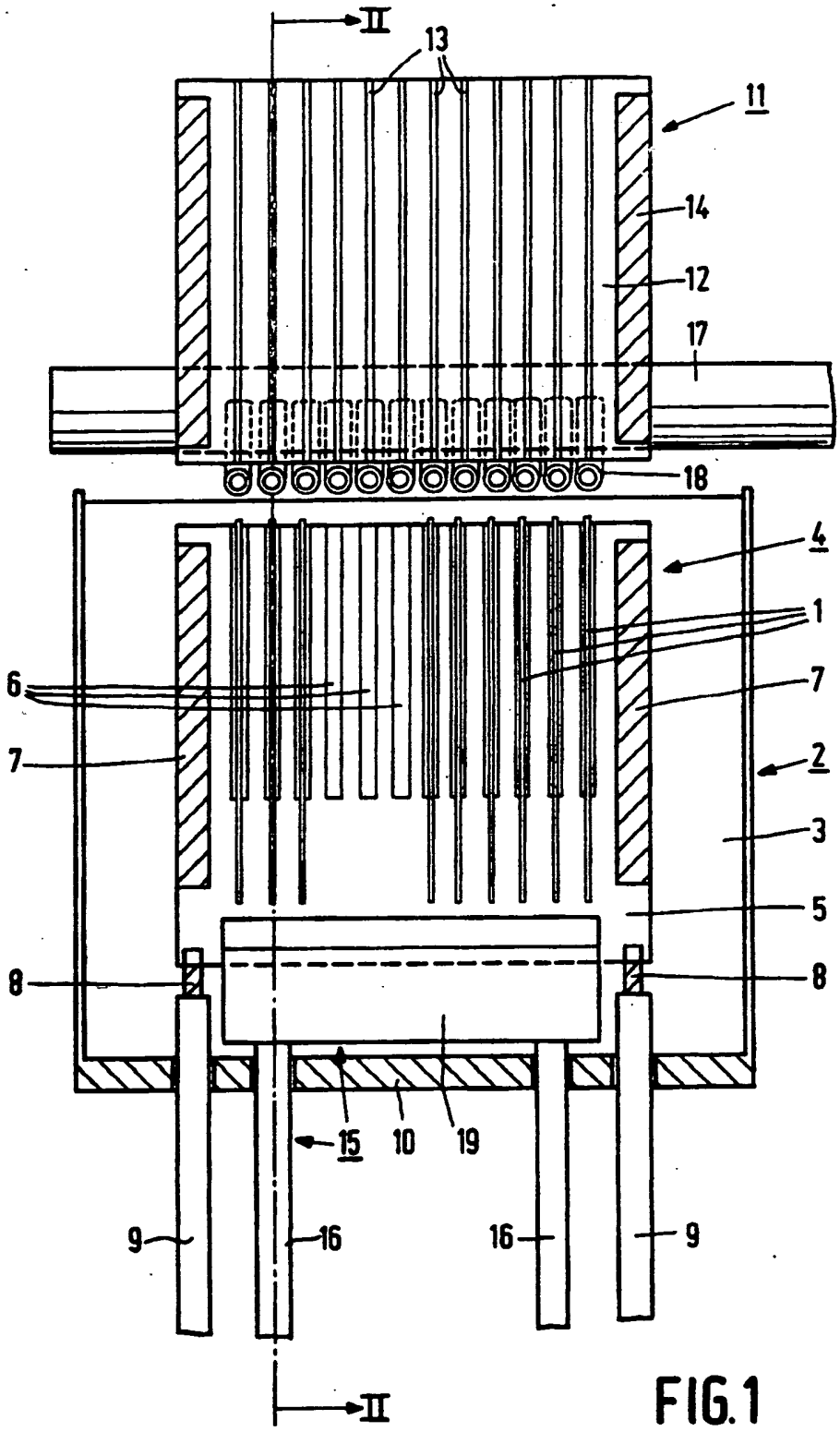

FIG.1

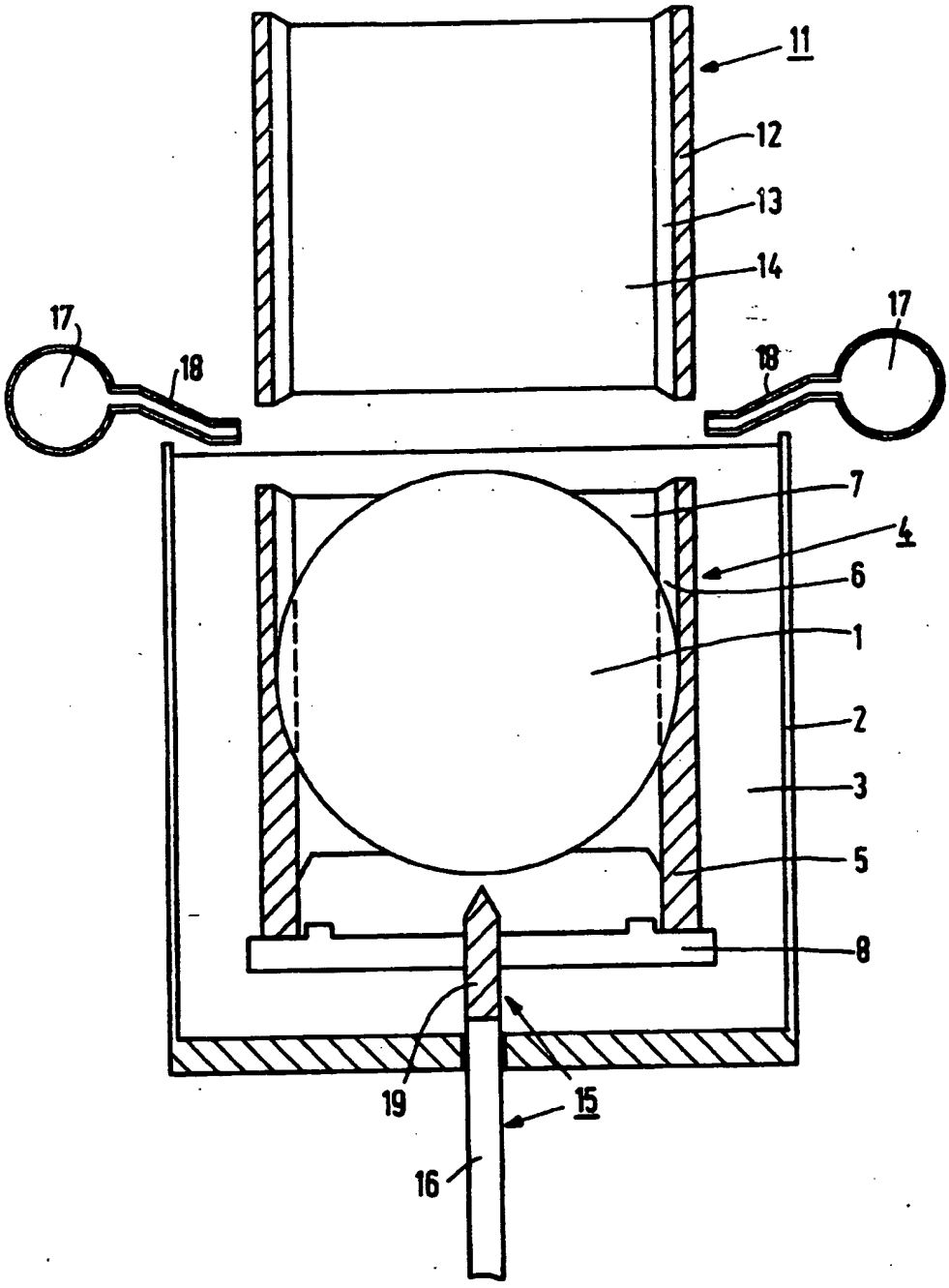

FIG.2

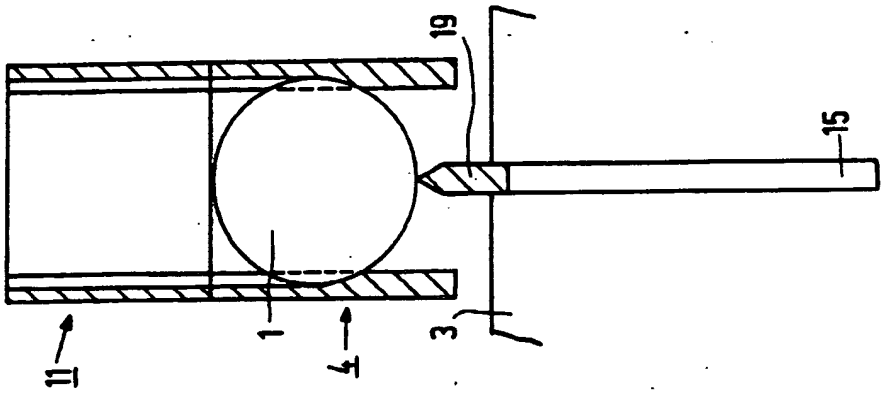

FIG.6

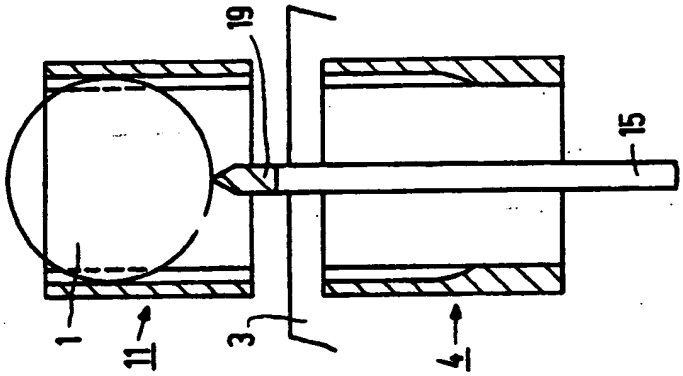

FIG.5

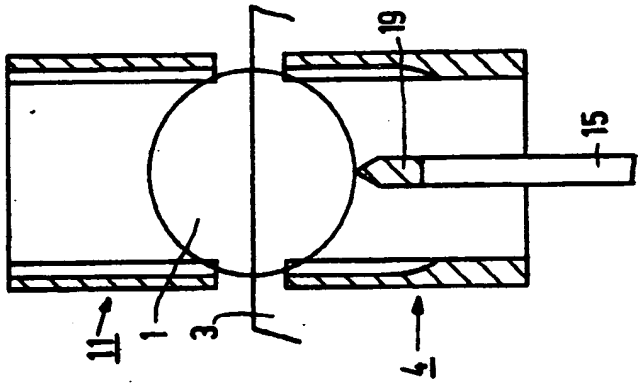

FIG.4

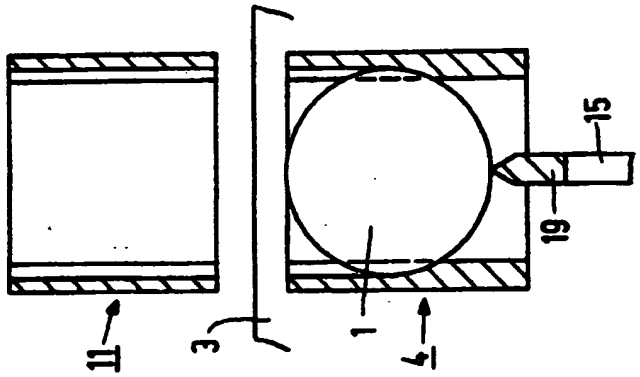

FIG.3

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EUROPEAN SEARCH REPORT

Application Number

EP 90 20 0409

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4746397 (NOBUHISA MAEDA ET AL.) * columns 3 - 6 * * column 7, lines 1 - 32; figures 2, 4 *	1, 2, 4, 5	H01L21/00
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 226 (E-272)(1663) 17 October 1984, & JP-A-59 107619 (HITACHI) 21 June 1984, * the whole document *	1	
A,D	US-A-4722752 (STECK R.B.) * abstract * * claim 4; figures 1-5 *	1, 8	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

H01L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 APRIL 1990	LOMMEL A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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